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IL 60563 (US). **DUBIN, Leonard** [US/US]; 5217 Arcadia, Skokie, IL 60077 (US). **LIN, Meijan, Linda** [US/US]; 8325 Wehrli Road, Naperville, IL 60540 (US). **TARABULSKI, Theodore, J.** [US/US]; Old Milltown Road, Brewster, NY 10509 (US).

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(74) Agent: **CARVIS, Thaddeus, J.; Ware, Fressola, Van der Sluys & Adolphson LLP, Bradford Green, Building Five, 755 Main Street, P.O. Box 224, Monroe, CT 06468 (US).**

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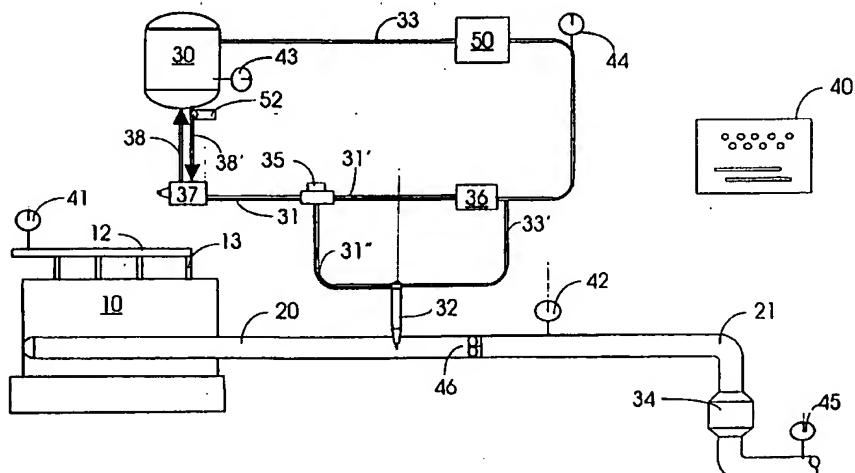
(71) **Applicant (for all designated States except US): CLEAN DIESEL TECHNOLOGIES, INC. [US/US]; Suite 702, 300 Atlantic Street, Stamford, CT 06901-3522 (US).**

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): BANKS, Rodney, Howard [US/US]; 1597 Whitley Road, Naperville,

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(54) Title: METHODS AND COMPOSITIONS FOR ASSURING REDUCTION OF NO_x EMISSIONS FROM AN ENGINE BY SELECTIVE CATALYTIC REDUCTION

[Continued on next page]



(57) **Abstract:** A reliable SCR system for reducing NO_x emissions from a lean-burn internal combustion engine (10) utilizes a chemical tagging reagent to assure proper usage of urea or other NO_x-reducing reagent (30). A reagent quality sensor (52) is provided to detect the tagging reagent and authenticate the NO_x-reducing reagent (30). The sensor (52) can desirably be used to determine feed rate to assure proper NO_x-reducing reagent feed rate, to thus prevent under dosing or over dosing, and can warn of a disruption in feed due to empty tank or stopped up feed line.



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DESCRIPTION

5 **METHODS AND COMPOSITIONS FOR ASSURING
REDUCTION OF NO_x EMISSIONS FROM AN
ENGINE BY SELECTIVE CATALYTIC REDUCTION**10 **Technical Field**

The invention relates to improving the reliability of a selective catalytic reduction (SCR) system for reducing NO_x emissions from lean-burn internal combustion engines, especially mobile engines.

15 Diesel and lean-burn gasoline engines provide advantages in fuel economy, but produce both NO_x and particulates during normal operation. When primary measures (actions that affect the combustion process itself, e.g., exhaust gas recirculation and engine timing adjustments) are taken to reduce one, the other is
20 usually increased. Thus, combustion conditions selected to reduce pollution from particulates and obtain good fuel economy tend to increase NO_x.

25 Current and proposed regulations challenge manufacturers to achieve good fuel economy and reduce particulates and NO_x. Lean-burn engines will be necessary to achieve the fuel economy objective, but the high concentrations of oxygen in the exhaust renders typical exhaust gas catalyst systems ineffective for reducing NO_x.

30 SCR (selective catalytic reduction) utilizes a reagent which, due to its ability to selectively reduce NO_x in the presence of a catalyst, can be used economically. It has been utilized for years to reduce NO_x emissions from stationary sources and is becoming a strong candidate for mobile sources. One possible hurdle to the

widespread adoption of this technology, however, is that from a regulatory standpoint there must be some means of assuring that the system is operating effectively. Another is the fact that it is not possible to measure NO_x emissions on a continuous and real-time basis.

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There is a current need for an effective answer to the regulatory and practical hurdles associated with SCR for mobile diesel and other lean-burn engines.

10 **Background Art**

Where SCR catalysts are employed to limit NO_x emissions from diesel engines, one has to deal with either the dangers of ammonia or satisfactorily deal with the risks of catalyst fouling. Aqueous urea and other liquid reagents have been 15 proposed to address the safety concerns associated with ammonia. In this regard, see R. J. Hulterman; A Selective Catalytic Reduction Of NO_x from Diesel Engines Using Injection Of Urea; Ph.D. thesis, September 1995; SAE Paper No. 970185, entitled "Transient Performance of a Urea DeNOx Catalyst for Low Emissions Heavy-Duty Diesel Engines"; U. S. Patent No. 5,431,893, to Hug, *et al.*; WO 97/01387 and 20 European Patent Application 487,886 A1. These references and those cited below are hereby incorporated by reference in their entireties.

Each of the points of caution by these references, especially for mobile sources, must be taken into account in developing a commercial SCR system 25 capable of widespread adoption. Further, there are concerns from a regulatory standpoint: principally, how can it be assured that the catalyst is being provided with an effective NO_x-reducing agent. The reagents cost money and there will always be an incentive for operators to either use a low-cost, noncomplying reagent or fail to refill when that is called for.

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The art is awaiting the development of a process apparatus and composition that would assure the use of an approved NO_x-reducing reagent comprising urea or other effective reagent in an SCR process.

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Disclosure of Invention

It is an object of the invention to provide a reliable SCR system for reducing NO_x emissions from an internal combustion engine.

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It is a yet further and more specific object of the invention to enable the use of urea in an SCR system that strongly discourages, if not effectively prevents, operator defeat.

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It is a yet further and still more specific object of one embodiment of the invention to enable the use of urea in an SCR system that strongly discourages or prevents operator defeat and enables integration with an engine management system (EMS).

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It is yet another specific object of the invention to provide a simple mechanical device for monitoring and maintaining the quality of the urea solution.

25

It is yet another specific object of the invention to provide a control system that senses failure of reagent quality and responds by switching to alternative NO_x control strategies to assure continuous NO_x reduction.

30

It is yet another object of the invention to provide a system that, while being specifically designed for urea solutions, can be employed with similar benefits for NO_x-reducing reagents other than urea, including hydrocarbon liquids, such as alcohols or the like.

It is yet another object of the invention to provide a system that can desirably be used to determine feed rate to assure proper NO_x-reducing reagent feed rate, to thus prevent under dosing or over dosing, and can warn of a disruption in feed due to an empty tank or stopped up feed line.

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It is yet another object of the invention to provide a system that achieves the above and other objectives by combining the technology of fluorometry with physical and/or chemical tests in a novel arrangement to detect attempts at NO_x control circumvention and preferably prevent such while providing adequate incentive for 10 voluntary compliance.

These and other objects are achieved by the present invention, which provides an improved method, a composition and an apparatus for assuring the reliability of a NO_x reduction SCR system.

15

The invention provides a method for assuring the presence of a NO_x-reducing reagent of predefined quality in a NO_x-reducing system, comprising: testing reagent solution for the presence and/or concentration of at least one fluorescent tracer; generating a sensor signal representative of the presence of the chemical tracer; 20 comparing the sensor signal to reference values; generating control signals representative of the results of the comparison; and, controlling the flow of urea solution responsive to the control signal.

Other parameters, such as level of the reagent can also be monitored by 25 fluorometry, physical and/or chemical means and employed to facilitate control.

In a preferred embodiment, if the quality of the urea solution fails testing, the injectors are shut off to prevent operation with a non-compliant solution. In this mode, the engine or other control system can provide a warning to the operator and will 30 preferably control engine operation to maintain low NO_x levels without the use of reagent, e.g., by exhaust gas recirculation, engine timing or derating to produce less

power. The system will preferably warn the operator of a potential loss of power and the operator will be required to replace the reagent with a standard reagent before normal operation will be resumed.

5 The apparatus in one embodiment comprises: a NO_x-reducing reagent quality sensor including a source of radiation within a defined range of wavelengths, supply means for feeding NO_x-reducing reagent to an exhaust system including an SCR reactor, and control means responsive to said quality sensor for controlling supply of NO_x-reducing reagent.

10

 The compositions according to the invention will comprise: a reagent effective for NO_x-reduction; and a chemical tracer which fluoresces when subjected to radiation within a defined range of wavelengths. In a preferred embodiment, the composition will also provide a chemical tracer designated by a particular catalyst manufacturer to assure that the composition is free of contaminants for the particular catalyst being employed.

Brief Description of the Drawing

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 The invention will be better understood and its advantages more apparent from the following detailed description, especially when read in light of the accompanying drawings, wherein:

25

 Figure 1 is a flow diagram showing principal components of one embodiment of the invention wherein a sensor is provided to test a NO_x-reducing reagent (such as aqueous urea solution) for the presence of a chemical tracer responsive to radiation within a defined range of wavelengths; and

30

 Figures 2 through 5 are logic diagrams of several preferred modes of operation according to the invention.

Detailed Description

In this description, the term "engine" is meant in the broad sense to include all combustors which combust liquid or gaseous hydrocarbon fuels to provide heat, 5 e.g., for direct or indirect conversion to mechanical or electrical energy. Internal combustion engines of the Otto, Diesel and turbine types, as well as burners and furnaces, are included and can benefit from the invention. However, since the problems and advantages of successful achievement of reliable NO_x reduction on diesel and other lean-burn engines are so pronounced, these engines are used 10 throughout this description for purposes of example. Stationary and mobile engines are contemplated.

In this description, the term "lean-burn engine" is meant to include engines that can be operated with an inlet oxygen concentration greater than the amount 15 required for stoichiometric (or chemically correct) combustion of a hydrocarbon fuel, e.g., at least 1% by weight excess oxygen.

The term "Diesel engine" is meant to include all compression-ignition engines, for both mobile (including marine) and stationary power plants and of the two-stroke 20 per cycle, four-stroke per cycle and rotary types.

The term "hydrocarbon fuel" is meant to include all of those fuels prepared from "distillate fuels" or "petroleum". Gasoline, jet fuel, diesel fuel, and various other distillate fuels are included. The term "distillate fuel" means all of those products 25 prepared by the distillation of petroleum or petroleum fractions and residues. The term "petroleum" is meant in its usual sense to include all of those materials regardless of source normally included within the meaning of the term, including hydrocarbon materials, regardless of viscosity, that are recovered from fossil fuels and specifically includes gaseous fuels, e.g., methane, propane, butane and the like.

The term "diesel fuel" means "distillate fuels" including diesel fuels meeting the ASTM definition for diesel fuels or others even though they are not wholly comprised of distillates and can comprise alcohols, ethers, organo-nitro compounds and the like (e.g., methanol, ethanol, diethyl ether, methyl ethyl ether, nitromethane).

- 5 Also within the scope of this invention, are emulsions and liquid fuels derived from vegetable or mineral sources such as corn, alfalfa, shale, and coal. These fuels may also contain other additives known to those skilled in the art, including dyes, cetane improvers, anti-oxidants such as 2,6-di-tertiary-butyl-4-methylphenol, corrosion inhibitors, rust inhibitors such as alkylated succinic acids and anhydrides,
- 10 bacteriostatic agents, gum inhibitors, metal deactivators, upper cylinder lubricants, antiicing agents and the like.

The term NO_x-reducing reagent is meant to include all of those that are effective for this purpose, especially those that can be stored in liquid form, e.g.,

- 15 hydrocarbons, such as straight and branched-chain aliphatic and/or aromatic hydrocarbons, including mixtures such as diesel fuel or any one or more of its constituents; oxygenated hydrocarbons, including aromatic compounds such as toluene, aliphatic compounds such as lower aliphatic alcohols, such as methanol, ethanol, propanol; and nitrogenous materials such as urea and aqueous ammonia
- 20 (NH₄OH).

The term "urea" is meant to encompass urea in all of its commercial forms, including those containing: ammelide; ammeline; ammonium carbonate; ammonium bicarbonate; ammonium carbamate; ammonium cyanate; ammonium salts of inorganic acids; ammonium salts of organic acids, including formic and acetic acid; biuret; cyanuric acid; isocyanic acid; melamine and tricyanourea. Typically, the commercial form of urea will consist essentially of urea, containing 95% or more urea or an aqueous solution containing urea of this purity.

- 30 Aqueous solutions of urea can be employed up to their solubility limits. Typically, the aqueous solution will contain from about 2 to about 65% reagent based

on the weight of the solution. Typical concentrations of urea are within the range of from about 25 to about 50%, e.g. from about 30 to about 35%. A preferred concentration for mobile uses is 32.5% urea which advantageously exhibits the lowest freeze point without precipitation of urea.

5

The urea or other reagent according to the invention will be prepared in its final form as a liquid (aqueous solution in the case of urea) in final form for use and will contain at least one tracer which fluoresces when subjected to radiation within a defined range of wavelengths, preferably in the visible range. It is preferred that the 10 fluorescent tracer be characterized by an excitation wavelength range of about 200 to 850 nanometers and a fluorescent "output" range of about 205 to 855 nanometers (nm). Non-interfering functional groups may be present in the fluorescent compound (sulfonate, hydroxyl, carboxylate, amino, amide, etc.). Aromatic rings may be present.

15

Desirably, the excitation and fluorescing wavelengths will be different. Exemplary of one preferred material of this type is Rhodamine B, CAS #81-88-9. This material can be excited at a wavelength of 554 nm (green) and emits at 580 nm (yellow). Rhodamine 6G is excited at 530 nm (green) and emits at a wavelength of 20 590 nm (yellow).

Another preferred fluorescent chemical tracer is 1,5-naphthalene disulfonic acid (NDSA) (excitation 290 nm, emission 330 nm), but a wide variety of fluorescent and other tracer or indicators can be employed to achieve the various objectives of the 25 invention. Yet another is pyrene tetrasulfonic acid (PTSA) which emits at 400 nm when excited at 365 nm.

The tracer can also be the noted nonylphenol ethoxylate surfactant. Among 30 other fluorescing surfactants are those such as octyl phenol ethoxylate, dialkylphenol ethoxylates and alkylnaphthylene ethoxylates. If the temperature of the treatment solution transmitted to the nozzles is exceptionally high, which it preferably isn't (the

temperature is preferably maintained at less than 100°C) then highly heat resistant fluorescent surfactants would be employed such as mentioned above. An independent fluorescent tracer could of course be used instead of one that is also a surfactant. Of course, if a surfactant is present, care should be exercised to avoid or 5 minimize interference and that fluorescence is sufficiently diverse to be distinguished.

To achieve the many objectives of the invention, other chemical tracers or indicators may also be chosen from a wide variety of chemicals including dyes and 10 transition metal-containing ions (colorimetry); also metal cations and anions (with ion selective electrodes as the instrument) which are inert in the NO_x treatment solution. See also, U.S. Patent No. 5,132,096 and U. S. Patent No. 5,277,185 for further 15 descriptions of chemistry and applications, for example. Two or more distinctive tracers (distinguishable on analysis) may be used.

15 There is reference above to selection of a fluorescent tracer in terms of possible high temperature of the treatment solution. High temperatures can cause a breakdown of tracers such as the ethoxylates listed above. In the instance of urea, high temperatures can occur because it sometimes becomes advantageous to heat 20 the urea solution above the boiling point in the mixer or at some other point prior to transmittal to the spray nozzles – in some instances this may occur due to process failure. This will encourage hydrolysis of urea, resulting in effective reaction products. The temperature may be as high as 100-300°C. Pressures in this case should be elevated sufficiently, if that is possible, to maintain a single-phase solution. 25 Therefore, in those instances where the treating solution can be expected to encounter high temperatures or intense shearing forces prior to reaching the point of introduction into the exhaust, highly heat and shear resistant tracers can be used such as those identified above. At lower temperatures where the alkylphenol ethoxylates are thermally stable and fulfill the requirements of an inert tracer, then 30 those compounds could be suitable for monitoring and/or controlling reagent supply.

In a preferred embodiment, the composition will also provide a chemical tracer designated by a particular catalyst manufacturer to assure that the composition is free of contaminants for the particular catalyst being employed. It may be useful to employ antifreeze materials and other reagents to enhance atomization (e.g., a 5 surfactant which may be an alkylphenol ethoxylate, or the like), maintain injectors free of deposits, or the like. Also, in the event that the sensor for the tracer is maintained within the tank, it can be useful to employ a detergent or other agent to maintain the sensor in clean and effective condition.

10 Figure 1 schematically shows a preferred embodiment incorporating the invention and its advantages. Briefly, diesel engine 10 is fed fuel via lines 12 and injectors 13. The engine produces exhaust gases containing NO_x that are passed through exhaust pipe 20. Urea solution is fed from vessel 30 to exhaust line 20 by one or more injectors, like 32. The exhaust gases are then passed through SCR 15 reactor unit 34. The process is preferably controlled by means of a controller 40, otherwise known as an onboard diagnostic unit (OBD) which can be either a separate unit or integrated with an engine management system (EMS). In an embodiment not shown, the urea solution is introduced into the exhaust between exhaust valves of the engine and an SCR (selective catalytic reduction) unit 34.

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Figure 1 shows a reagent injector system employing a feed line, e.g., a common rail 31, with a return to the supply via spill line 33. This system maintains a continuous flow of reagent between storage vessel 30 and injector 32. The term injector is used herein to describe any device capable of controlling flow of urea 25 solution from the rail 31 to the exhaust gases. The injector can be either a high-pressure or a low-pressure device as will be explained in more detail below.

30 Among the low-pressure devices are any of the available low-pressure liquid distribution means, such as a mechanical atomizer of the type employed to inject liquid fuels for internal combustion engine use, spray paints, a sonic atomizer, a simple valve extending to a tube with a dispersion device comprising a plurality of

orifices to provide a fine spray, or a pintle-controlled nozzle. Preferred injectors of this type will operate at reasonably elevated pressures of from about 10 to about 100 psig, e.g., from about 30 to 50 psig. High-pressure units can also be employed. Air-powered nozzles can be employed, but it is preferred to operate them with a 5 minimum of air to reduce the cost of the equipment and the effect air has on cooling the exhaust. In circumstances where neither air supply nor its cooling effect are unacceptable design compromises, air can be employed to cool the injector and/or aid injection of urea solution.

10 One preferred form of injector is illustrated in U. S. Patent Application No. 09/164,304, filed October 1, 1998, and entitled FLUID-COOLED INJECTOR. This injector has a pintle controlled injection orifice and provides a impact plate directly outside the orifice such that the spray from the orifice will impact the plate and become rapidly, finely dispersed. A solenoid can be employed to electrically operate 15 this injector and other preferred forms. Both the frequency of opening and the duration of any open position can be controlled. The percentage open time can conveniently be from 0 to 80%. The frequency can conveniently be from 5 to 30 hertz. It will be understood that a wide range of other values can be employed. It is an advantage of the invention that control of the injector is so flexible and can be so 20 rapid as to facilitate rapid adjustment to transient engine operating conditions.

In-line mixing means are preferably employed to assure good distribution of urea solution within the exhaust gases, especially when low-pressure injectors are employed. Distribution is important because high concentrations of urea solution can 25 cause localized cooling and this can result in droplets of water or particles of urea or pyrolysis products surviving and then impacting the SCR catalyst. One suitable device is shown as a propeller 46. Alternatively, a foraminous body, mist eliminator, static mixer, particulate trap or other like device having a mixing capability can be employed. Figure 1 also shows bend 21 in exhaust pipe 20, to act as a guard 30 against liquid or solid urea or urea residues from contacting the catalyst in SCR reactor 34.

The embodiment illustrated in Figure 1 includes a rail pressure sensor 35 and a pressure-regulating valve 36. Pressure within the rail and return lines by valve 36 and pump 37, in response to control signals provided by controller 40. It will be 5 noted that pressurized lines 31, 31' and 31" are shown in the Figure as darker than the unpressurized return lines 33 and 33'. Optionally, a heat exchanger 50 can be employed in line 33 to cool the urea solution in the case of overheating or heat it when ambient temperatures are very low. Lines 38 and 38' between the pump 37 and vessel 30 provide agitation as needed to the urea solution.

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It is possible, and in some cases desirable to enclose a flow control and sensor module within the tank 30 to perform one or more of the following functions: measure reagent level, sense reagent temperature, sense reagent quality, a pump, a heater. A module of this type can be connected to a suitable controller by one or 15 more electrical harnesses.

Controller 40 is preferably integrated with an EMS for the engine 10 to avoid the need for several different controllers and to utilize existing wiring harnesses and sensors to the extent possible. Various sensors are shown and function to sense 20 various operation parameters and generate operation signals representative of the sensed parameters. The operation signals are then sent to the controller, which compares them to reference values, computes one or more control signals and sends the control signals to one or more devices being controlled.

25 Figure 1 shows sensor 41 for engine, sensor 42 for exhaust gas temperature, sensor 43 for urea level in vessel 30, and sensor 44 for the temperature of the urea solution in return line 33. Engine load, as represented by one or more suitable parameters, such as fuel flow, engine speed, throttle position or injection system settings, is a key parameters, and one of these or like factor can be monitored to 30 determine the amount of NO_x being generated and the need for reagent feed to the heating unit or its hydrolysis products fed to the exhaust gases. Optional sensors,

such as sensor 45 for residual NO_x concentrations, can be employed for feedback control to the extent that such is practical. The Figure also shows in dotted lines operation signals being sent to the controller and control signals being sent to controlled devices.

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The temperature of the urea solution throughout the system is maintained at a value sufficiently low that it is not permitted sufficient time at elevated temperature to hydrolyze the urea to such an extent that solids precipitate (e.g., below about 140°C). The injector 32 will tend to heat up as the temperature of the exhaust gases 10 rises after startup to within the range of from about 300° to about 650°C at high load for some engines. Unless precautions are taken, the high temperature will cause hydrolysis of the urea before injection – causing the hydrolysis products to precipitate due to their lower solubility than urea. The invention circulates the urea solution continuously from vessel 30 through lines 31 and 33 (and associated lines, as 15 controlled) to provide cooling to the injector. It is practical with suitable controls to let the temperature of the solution rise to between 105°C and 130°C when the system is pressurized to the saturated vapor pressure for the temperatures involved. Because the residence time on the spill line is short, the urea solution may be allowed to reach higher temperatures without reaching the solubility limit for 20 hydrolysis products. An auxiliary heating means (not shown) can be employed in the vessel 30 or elsewhere in the feed or return system to achieve a desired temperature.

Line 33 can be eliminated in embodiments where separate cooling means are 25 provided for the injector. A reagent quality sensor 52 is conveniently located on the feed line 38'.

The exact nature of this sensor 52 will depend on the reagent selected, but will preferably comprise a light emitting diode of suitable color to excite a fluorescent 30 indicator and a photodiode receiver to sense the emitted light and convert the received light signal and convert it to a electronic control signal. For example, where

the reagent is Rhodamine B, a green light emitting diode (554nm, typical), such as made by AND, Inc., for example, can be used to excite the Rhodamine B, which emits at 580 nm, can be employed.

5 According to another procedure, a sample is taken from the line 38' and is delivered to an analyzer 52. In the instance of analyzing fluorescent tracer, the analyzer may be characterized by a cylinder or tube of a material which is transparent to light generated by a light source therein, e.g., quartz in the case ultraviolet. The light source will operate at the wavelength necessary to excite the
10 fluorescent surfactant or other fluorescent tracer compound as disclosed hereinafter. Other forms of actinic radiation could be used to excite (energize) the fluorescent compound.

At a 90° angle from the light source is a transducer which transforms the
15 fluorescent light emitted by or from the activated sample into a signal which may be DC voltage, DC amperage, pulse frequency and the like as an analog of the tracer concentration and therefore an analog of the chemical treatment concentration of which urea concentration is an example. This mode of transformation and analog signal generation is disclosed for example in U.S. Pat. Nos. 4,992,380 and
20 5,041,386.

The analog signal will be used to control equipment which feeds the NO_x-reducing reagent. The analog signal can also be used in several ways to produce an intelligible record of the chemical treatment concentration thus analyzed.

25 Thus, by using a standard concentration for the fluorescent tracer relative to urea concentration, the system can be programmed to test for low concentration, over dosing, or absence of reagent due to being empty or subject to a flow blockage. A sample of the treatment solution (in line 38' or at other convenient location) being
30 pumped to a suitable injector or spray nozzle can be excited at the wavelength required to produce fluorescent intensity. The intensity of fluorescence thus produced for the sample can be compared (percentage-wise for example) to the

known intensity of the calibration standard. By comparison, then, it can be determined how the treatment solution compares with the standard in terms of concentration of the treating agent. By such comparison, it can be determined whether the feed rate should be altered from the standpoint of active reactant 5 (product) concentration, either more or less, or allowed to stand as it is. The comparison may be an intermittent one, or continuous.

As the concentration of the tracer, e.g., in parts per million of fluorescent tracer, decreases due to dilution water added to the concentrated chemical treatment 10 solution containing the tracer, the fluorescent intensity of the sample decreases proportionally when considering (taking) the standard (e.g. 1.0 ppm tracer) as 100%. The chemical treatment (effective reagent) concentration varies the same way. When a low concentration is noted, there are several possible control responses, including increasing the flow proportionally or stopping flow and converting to a different NO_x 15 control mode.

This can also be used to deter or prevent unauthorized dilution with distilled or deionized water. As will be discussed later, diluting the solution with tap water can also be detected. It can also detect overdosing, which can also cause problems such 20 as emission of ammonia.

Controller 40 can be integrated with an EMS for the engine 10 to avoid the need for several different controllers and to utilize existing wiring harnesses and sensors to the extent possible. Alternatively, a dedicated controller including the 25 features necessary for SCR can be employed using either dedicated sensors or sharing where possible with the EMS. Various sensors are shown and function to sense various operation parameters and generate operation signals representative of the sensed parameters. The operation signals are then sent to the controller, which compares them to reference values, computes one or more control signals 30 and sends the control signals to one or more devices being controlled.

Responsive to the control signals, the flow of urea solution is controlled, either clearing it from injectors and/or feed lines or injecting it into the exhaust gases at a rate sufficient for SCR; and passing the exhaust gas through an SCR reactor.

5 Other parameters, such as pressure in the vessel and/or feed lines can also be monitored and employed to facilitate control. Any or all of these control parameters can be processed by dedicated signal processors or by a main engine control unit where direct benefit can be had of reference to a comprehensive engine parameter map.

10 The preferred compositions will contain scale control compositions as necessary to combat hardness in dilution water (e.g., non deionized water), if used. Also, cleaners and surfactants can be employed to maintain suitable flow and freedom from deposits on sensors.

15 A principal advantage of the invention is that in addition to checking for the presence of the required levels of quality reagent, certain contaminants can be sensed and made part of the control scheme in addition to the fluorescent chemical. Other parameters, such as level of the reagent and/ or the presence of contaminants 20 can also be monitored by fluorometry, physical and/or chemical means and employed to facilitate control. For example, chlorine is detrimental to many catalysts and can be made the subject of control. For example, one embodiment provides a sensor, e.g., an ORP probe (oxidation-reduction potential which measures the potential of chlorine species on the surface of a noble metal electrode vs. a 25 reference electrode) for detecting the presence of harmful chlorine concentrations. This is important because some operators might attempt to dilute the standard reagent with tap water. This, in addition to reducing the reagent concentration reaching the catalyst, would deliver chlorine to it and possibly harm its long-term functionality. Chlorine can have a number of harmful effects: it can corrode the 30 exhaust system including catalyst canisters, it can degrade the catalyst support and it can reduce the vapor pressure of catalyst metals.

In addition to chlorine, other contaminants of possible importance are phosphorous, lead, arsenic, zinc, sulfur, vanadium and oily components that might reduce the effectiveness of the sensors.

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In the preferred embodiment, a heater is provided for temperature maintenance of the urea solution.

The invention thus provides a method for assuring the presence of a NO_x -reducing reagent of predefined quality in a NO_x -reducing system, comprising: testing reagent solution for the presence of at least one fluorescent tracer; generating a sensor signal representative of the presence of the chemical tracer; comparing the sensor signal to reference values; generating control signals representative of the results of the comparison; and, controlling the flow of urea solution responsive to the control signal.

In a preferred embodiment, if the quality of the urea solution fails testing, the injectors are shut off to prevent operation with a defective solution. In this mode, the engine or other control system can provide a warning to the operator and will preferably control engine operation to maintain low NO_x levels without the use of reagent, e.g., by exhaust gas recirculation, engine timing or derating to produce less power. The system will preferably warn the operator of a potential loss of power and the operator will be required to replace the reagent with a standard reagent before normal operation will be resumed. Several preferred logic diagrams for this are shown in Figures 2 through 5.

The apparatus in one embodiment comprises: a NO_x -reducing reagent quality sensor including a source of radiation within a defined range of wavelengths, supply means for feeding NO_x -reducing reagent to an exhaust system including an SCR reactor, and control means responsive to said quality sensor for controlling supply of NO_x -reducing reagent.

The compositions according to the invention will comprise: a reagent effective for NO_x-reduction; and a chemical tracer that fluoresces when subjected to radiation within a defined range of wavelengths. In a preferred embodiment, the composition 5 will also provide a chemical tracer designated by a particular catalyst manufacturer to assure that the composition is free of contaminants for the particular catalyst being employed.

In a preferred embodiment, an excessively low temperature for the urea in the 10 storage vessel, will cause a heater to start to maintain the temperature of the solution within a desired range. It is preferred in this mode of operation, to also monitor the availability of auxiliary or battery power to run the heater. If it determined that insufficient power is available, injectors and feed lines will be drained to avoid freezing. In this mode, the engine control system can provide a warning to the 15 operator and will preferably control engine operation to maintain low NO_x levels without the use of reagent, e.g., by exhaust gas recirculation, engine timing or derating to produce less power.

In accord with the preferred mode of operation, the quality of the urea solution 20 will be monitored and if it fails testing on one or more criteria, the injectors are preferably stopped. In this mode, the engine control system can provide a warning to the operator and will preferably control engine operation to maintain low NO_x levels without the use of reagent, e.g., by exhaust gas recirculation, engine timing or derating to produce less power. Before the SCR system can be operated again, and 25 full engine power restored, the anomaly must be corrected.

In another embodiment, however, the return lines 33 and 33' are not employed or are not the sole means for temperature maintenance. In this embodiment, heat exchange fluid such as air or engine coolant can be passed in 30 heat exchange contact with the injector. Permissibly, in this embodiment, the temperature of the urea solution can be allowed to rise above 100°C as long as the

urea solution is maintained at a pressure above the saturation vapor pressure at the temperature.

The SCR catalyst used is one capable of reducing the effluent nitrogen oxides 5 concentration in the presence of ammonia. These include, for instance, activated carbon, charcoal or coke, zeolites, vanadium oxide, tungsten oxide, titanium oxide, iron oxide, copper oxide, manganese oxide, chromium oxide, noble metals such as platinum group metals like platinum, palladium, rhodium, and iridium, or mixtures of these. Other SCR catalyst materials conventional in the art and familiar to the skilled 10 artisan can also be utilized. These SCR catalyst materials are typically mounted on a support such as a metal, ceramic, zeolite, or homogeneous monolith, although other art-known supports can also be used.

Among the useful SCR catalysts are those representative prior art processes 15 described below. Selective catalytic reduction processes for reducing NO_x are well known and utilize a variety of catalytic agents. For instance, in European Patent Application WO 210,392, Eichholtz and Weiler discuss the catalytic removal of nitrogen oxides using activated charcoal or activated coke, with the addition of ammonia, as a catalyst. Kato *et al.* in U.S. Patent 4,138,469 and Henke in U.S. 20 Patent 4,393,031 disclose the catalytic reduction of NO_x using platinum group metals and/or other metals such as titanium, copper, molybdenum, vanadium, tungsten, or oxides thereof with the addition of ammonia to achieve the desired catalytic reduction. See also EP 487,886, which specifies a V₂O₅/WO₃/TiO₂ catalyst with a working range of 220 to 280°C. Other catalysts based on platinum can have 25 operating temperatures even lower, e.g., down to about 180°C.

Another catalytic reduction process is disclosed by Canadian Patent 1,100,292 to Knight, which relates to the use of a platinum group metal, gold, and/or silver catalyst deposited on a refractory oxide. Mori *et al.* in U.S. Patent 4,107,272 30 discuss the catalytic reduction of NO_x using oxysulfur, sulfate, or sulfite compounds

of vanadium, chromium, manganese, iron, copper, and nickel with the addition of ammonia gas.

In a multi-phased catalytic system, Ginger, in U.S. Patent 4,268,488, 5 discloses exposing a nitrogen oxides containing effluent to a first catalyst comprising a copper compound such as copper sulfate and a second catalyst comprising metal combinations such as sulfates of vanadium and iron or tungsten and iron on a carrier in the presence of ammonia.

10 The effluent to which the urea has been introduced is preferably passed over the SCR catalyst while the effluent is at a suitably high temperature, typically between about 180°C and about 650°C, e.g., at least about 300°C. In this manner, the active species present in the effluent due to hydrolysis and gasification of the urea solution most effectively facilitates the catalytic reduction of nitrogen oxides.

15 The effluent will contain an excess of oxygen. Use of the present invention with any of the above SCR catalysts (the disclosure of which are specifically incorporated by reference) reduces or eliminates the requirement for the transport, storage and handling of large amounts of ammonia or ammonium water.

20 The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading this description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present 25 invention which is defined by the following claims. The claims cover the indicated components and steps in all arrangements and sequences which are effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

CLAIMS

1. A method for assuring the presence of a NO_x-reducing reagent of predefined quality in a NO_x-reducing system, comprising:
 - testing reagent solution for the presence of at least one fluorescent tracer;
 - generating a sensor signal representative of the presence of the chemical tracer;
 - comparing the sensor signal to reference values;
 - generating control signals representative of the results of the comparison; and,
 - controlling the flow of urea solution responsive to the control signal.
2. A method according to claim 1 wherein other parameters, such as level of the reagent can also be monitored by fluorometry, physical and/or chemical means and employed to facilitate control.
3. A method according to claim 1 wherein, if the quality of the urea solution fails testing, reagent injectors are shut off to prevent operation with a defective solution.
4. A method according to claim 3 wherein, the engine or other control system can provide a warning to the operator and will preferably control engine operation to maintain low NO_x levels without the use of reagent, e.g., by exhaust gas recirculation, engine timing or derating to produce less power.
5. A method according to claim 3 wherein the system will preferably warn the operator of a potential loss of power and the operator will be required to replace the reagent with a standard reagent before normal operation will be resumed.
6. A method for assuring the correct dosage of a NO_x-reducing reagent of predefined quality in a NO_x-reducing system, comprising:

22

testing reagent solution for the presence of at least one fluorescent tracer;

generating a sensor signal representative of the concentration of the chemical tracer;

comparing the sensor signal to reference values;

generating control signals representative of the results of the comparison; and, controlling the flow of urea solution responsive to the control signal.

7. A method according to claim 7 wherein other parameters, such as level of the reagent can also be monitored by fluorometry, physical and/or chemical means and employed to facilitate control.

8. A method according to claim 7 wherein, if the quality of the urea solution fails testing, reagent injectors are shut off to prevent operation with a defective solution.

9. A method according to claim 9 wherein, the engine or other control system can provide a warning to the operator and will preferably control engine operation to maintain low NO_x levels without the use of reagent, e.g., by exhaust gas recirculation, engine timing or derating to produce less power.

10. A method according to claim 9 wherein the system will preferably warn the operator of a potential loss of power and the operator will be required to replace the reagent with a standard reagent before normal operation will be resumed.

11. An apparatus for assuring the presence of a NO_x-reducing reagent of predefined quality in a NO_x-reducing system, comprising:

a NO_x-reducing reagent quality sensor including a source of radiation within a defined range of wavelengths,

supply means for feeding NO_x-reducing reagent to an exhaust system including an SCR reactor, and

23

control means responsive to said quality sensor for controlling supply of NO_x-reducing reagent.

12. A composition for assuring the presence of a NO_x-reducing reagent of predefined quality in a NO_x-reducing system, comprising:

- a reagent effective for NO_x-reduction; and
- a chemical tracer which fluoresces when subjected to radiation within a defined range of wavelengths.

13. A composition according to claim 13, which also includes a chemical tracer designated by a particular catalyst manufacturer to assure that the composition is free of contaminants for the particular catalyst being employed.

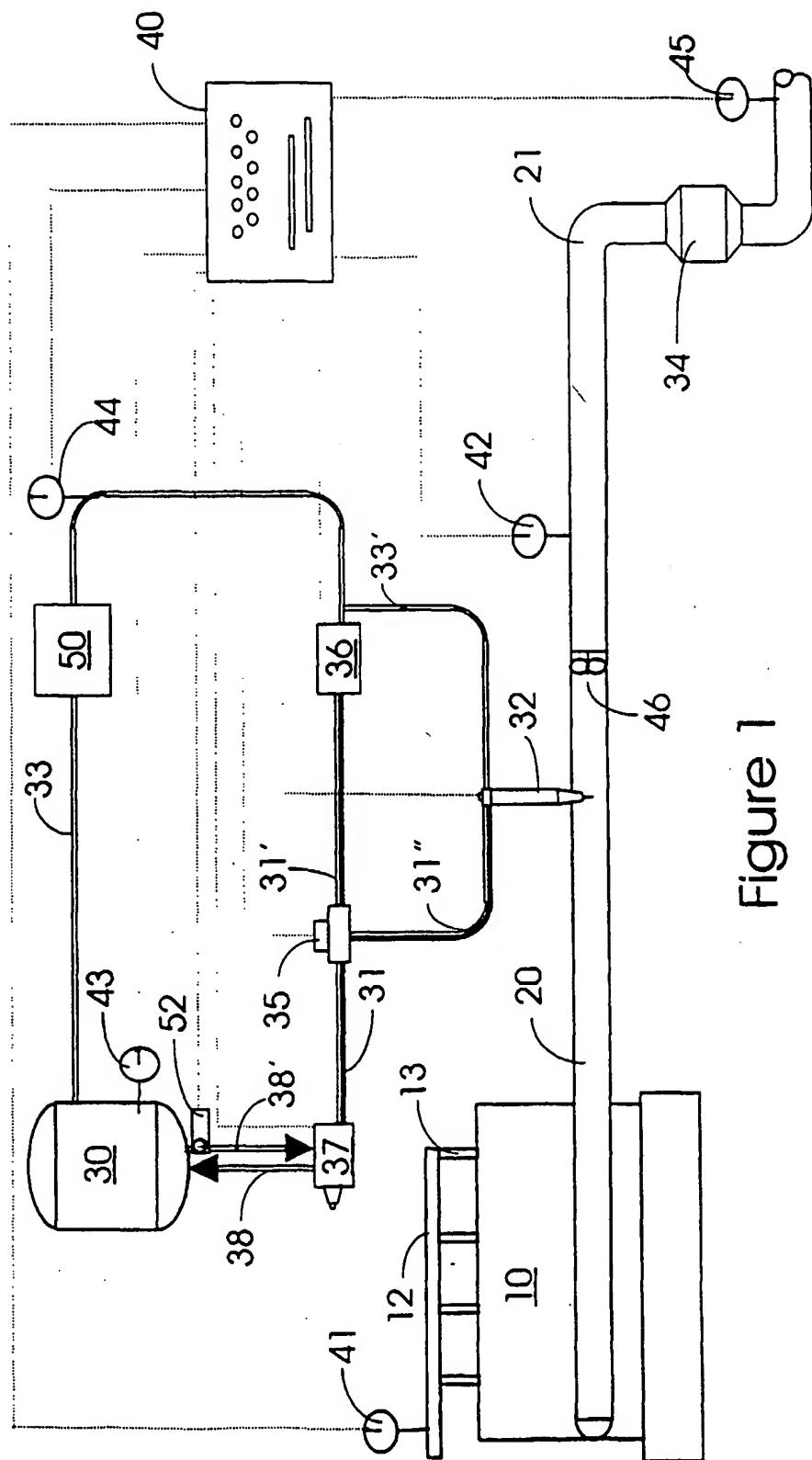


Figure 1

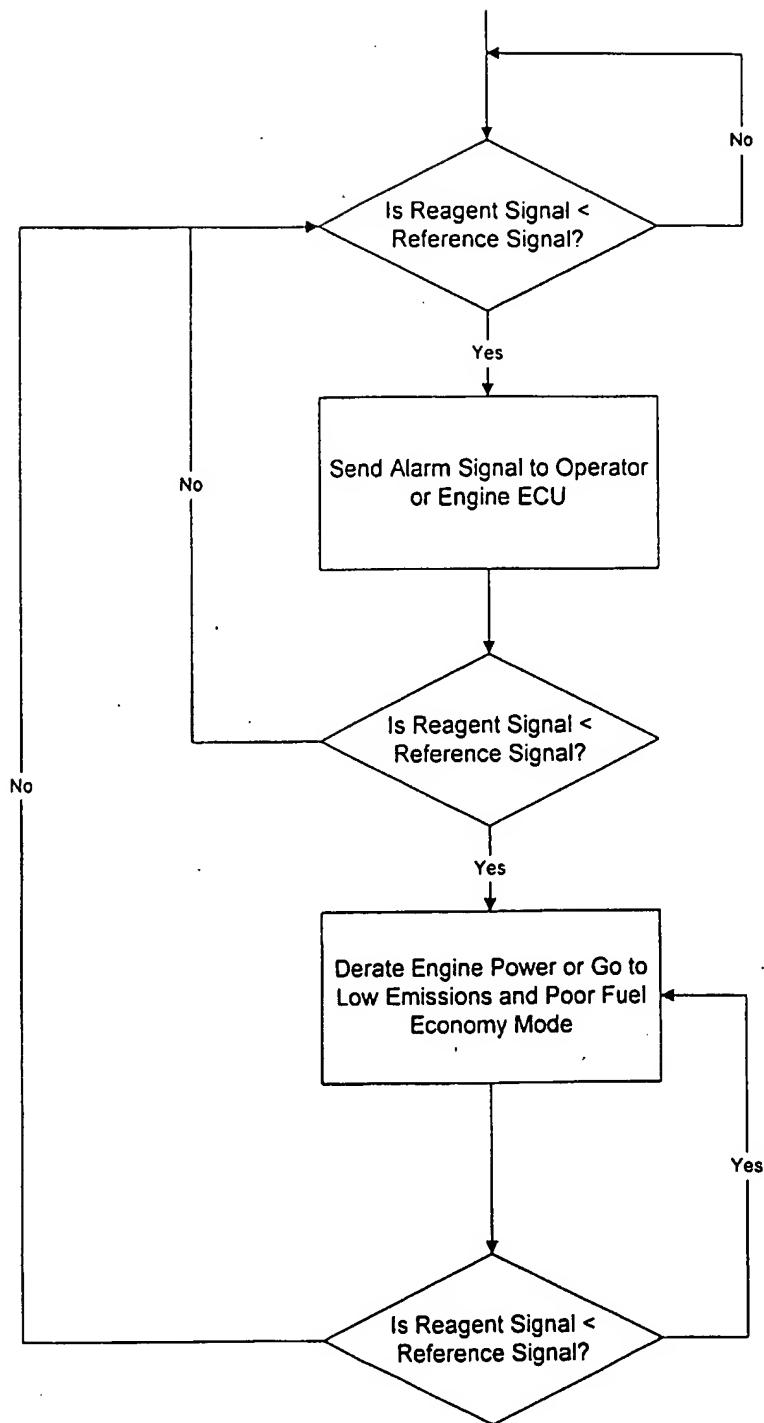


Figure 2

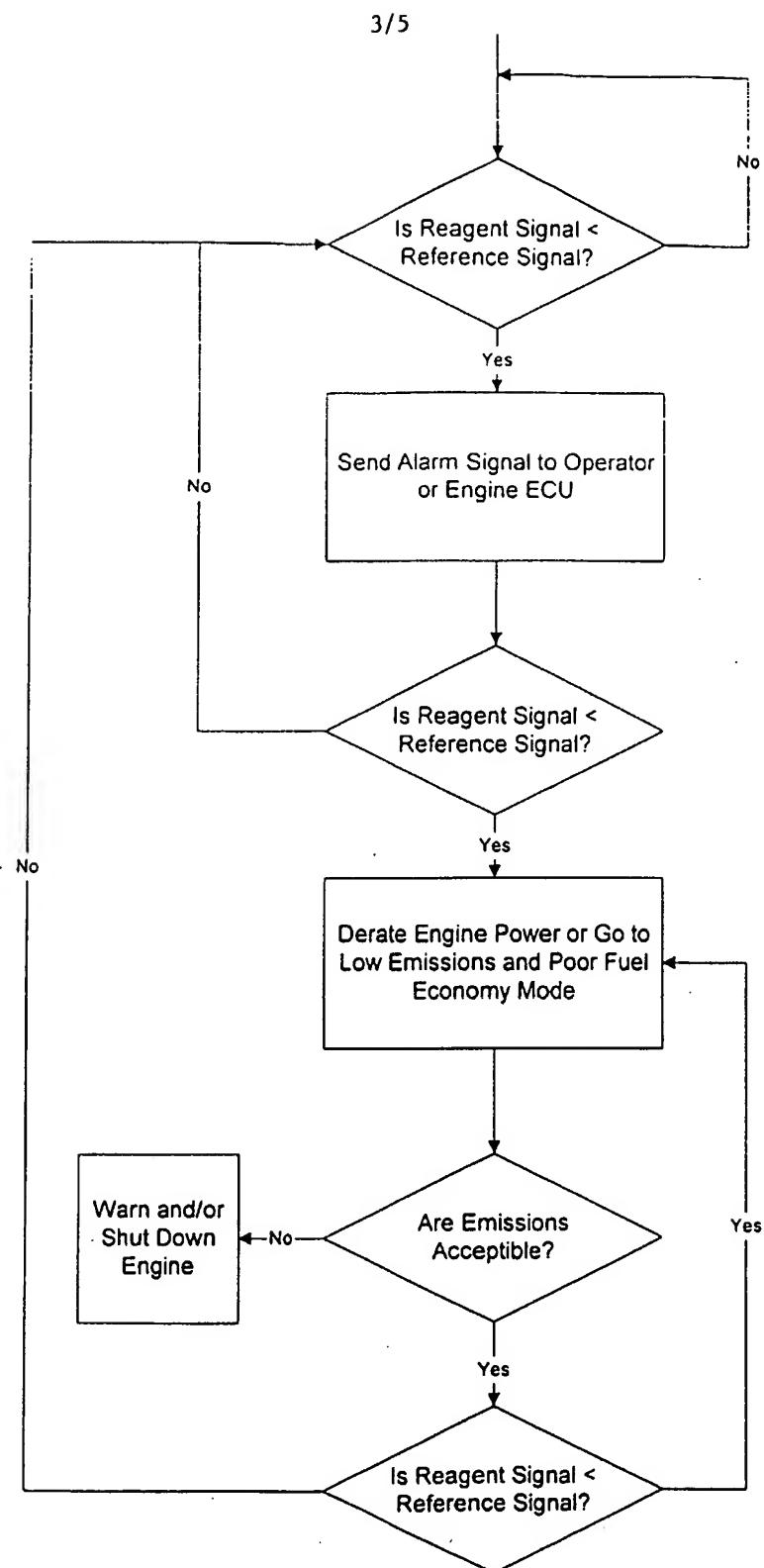


Figure 3

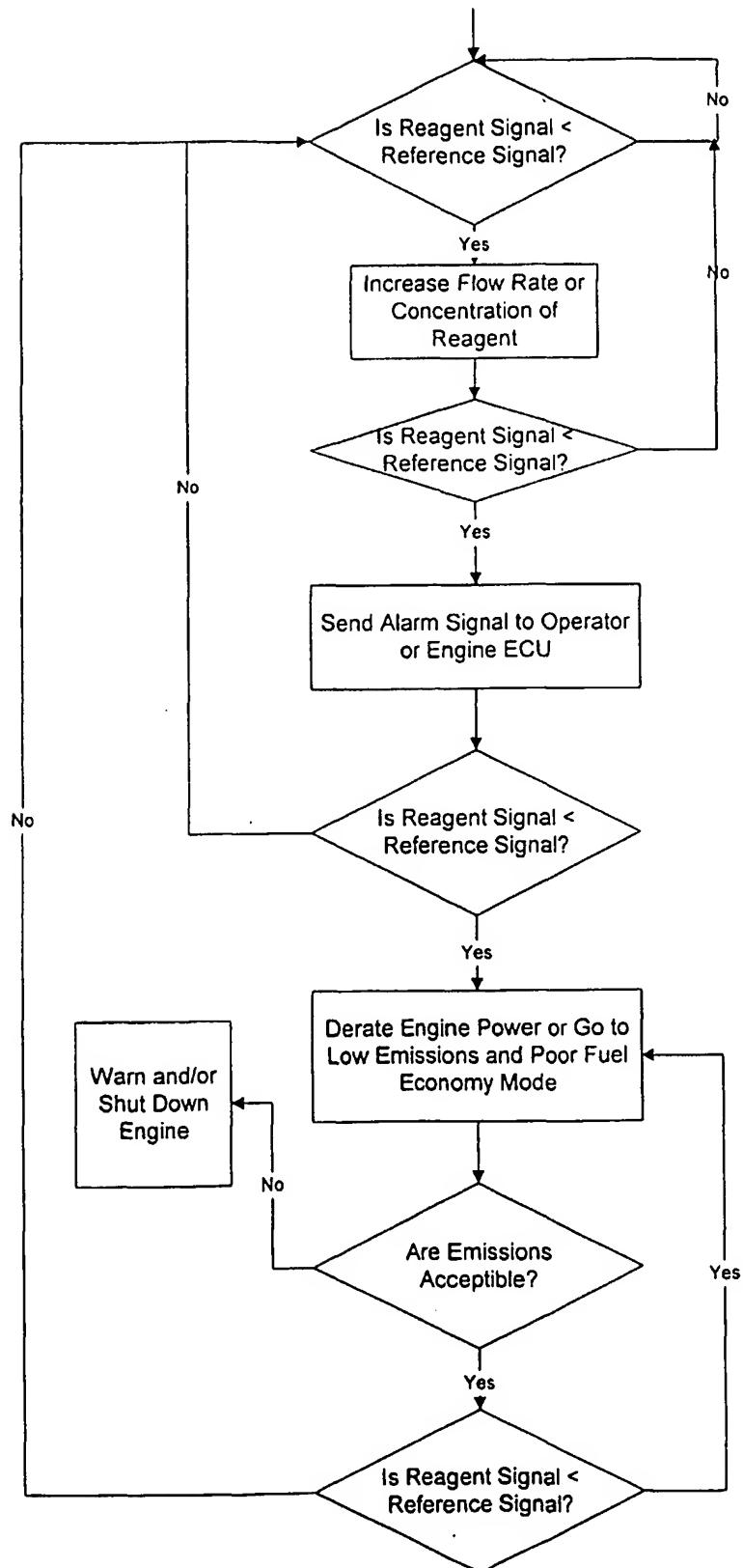


Figure 4

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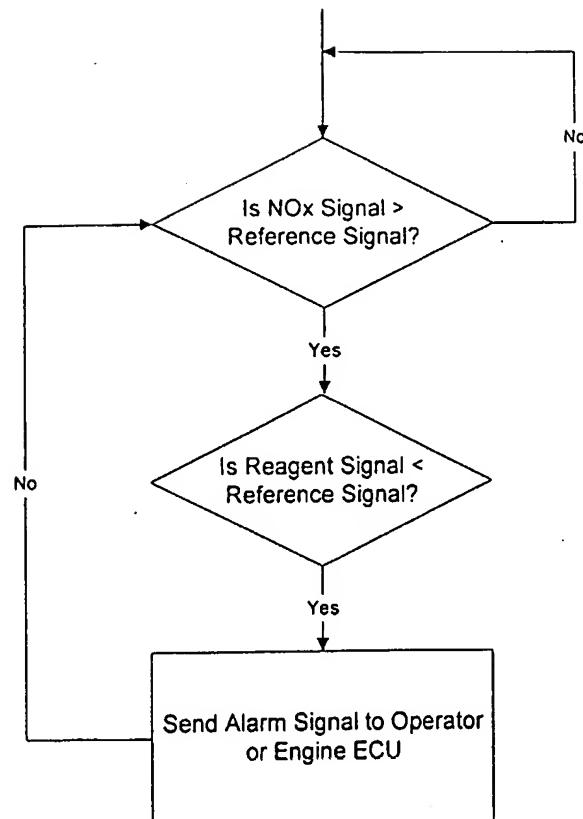


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/40111

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G01N 21/76, 37/00

US CL :436/43, 50, 55, 56, 108, 164, 166, 172

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/43, 50, 55, 56, 108, 164, 166, 172

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
| X | US 5,441,713 A (DUBIN et al) 15 August 1995, see column 14. | 13 |
| X | US 5,277,135 A (DUBIN et al) 11 January 1994, see entire document. | 13 |
| --- | | ----- |
| Y | | 1-12,14 |
| Y,P | US 6,063,350 A (TARABULSKI et al) 16 May 2000, see entire document. | 1-14 |
| Y,P | US 5,976,475 A (PETER-HOBLYN et al) 02 November 1999, see entire document. | 1-14 |
| Y,P | US 5,968,464 A (PETER-HOBLYN et al) 19 October 1999, see entire document. | 1-14 |
| Y,P | US 5,809,775 A (TARABULSKI et al) 22 September 1999, see entire document. | 1-14 |

| | | | |
|-------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <input checked="" type="checkbox"/> | Further documents are listed in the continuation of Box C. | <input type="checkbox"/> | See patent family annex. |
| • | Special categories of cited documents: | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| "A" | document defining the general state of the art which is not considered to be of particular relevance | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| "E" | earlier document published on or after the international filing date | "Y" | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "L" | document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "&" | document member of the same patent family |
| "O" | document referring to an oral disclosure, use, exhibition or other means | | |
| "P" | document published prior to the international filing date but later than the priority date claimed | | |

| | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| Date of the actual completion of the international search 13 SEPTEMBER 2000 | Date of mailing of the international search report 18 OCT 2000 |
| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230 | Authorized officer ARLEN SODERQUIST Telephone No. (703) 308-0661 DEBORAH THOMAS PARALEGAL SPECIALIST |

INTERNATIONAL SEARCH REPORT

| |
|-------------------------------------------------|
| International application No. PCT/US00/40111 |
|-------------------------------------------------|

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y,P | US 5,809,774 (PETER-HOBLYN et al) 22 September 1999, see entire document. | 1-14 |
| Y | T. Morimune et al, "Study of Catalytic Reduction of NOx in Exhaust Gas from a Diesel Engine" Experimental Thermal and Fluid Science 1998, Vol. 18, pages 220-230, see entire document. | 1-14 |
| Y | WO 97/36676 A (CLEAN DIESEL TECHNOLOGIES, INC.) 09 October 1997, see entire document, | 1-14 |
| Y | H. T. Hug et al, "Off-Highway Exhaust Gas After-Treatment: Combining Urea-SCR, Oxidation Catalysis and Traps" Soc. Automot. Eng., SP 1993, Vol. SP-943, pages 143-154, see entire document. | 1-14 |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/40111

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/40111

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

STN search in REGISTRY and CA files.

search terms: urea, nitrogen dioxide, nox, no2, reduc?, eliminat?, cataly?, scr, nh2conh2, fluoresc?, trace, tracer, label?, mark?, aqueous, solution, mixtrue, engine, tamper?, quality

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s)1-5, drawn to a method of assuring the presence of a nitrogen oxides reducing reagent.

Group II, claim(s) 7-11, drawn to a method for assuring the correct dosage of a nitrogen oxides reducing agent.

Group III, claim(s) 12, drawn to an apparatus for assuring the presence of a nitrogen oxides reducing agent.

Group IV, claims 13-14, drawn to a composition for assuring the presence of a nitrogen oxides reducing agent.

The inventions listed as Groups I-IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature is the presence of the tracer in the reagent composition which is clearly anticipated by the cited Dubin references (US 5,277,135 and 5,441,713).